

THESE

PRESENTEE A

L'UNIVERSITE DE PROVENCE

PAR

Jean-Pierre AYCARD

POUR OBTENIR LE GRADE DE
DOCTEUR ES-SCIENCES PHYSIQUES

INTERACTIONS GAUCHES EN SERIES CYCLOHEXANIQUE ET CYCLOHEXENIQUE

(annexes)

SOUTENUE LE 20 DECEMBRE 1974 DEVANT LA COMMISSION D'EXAMEN :

MM. H. BODOT

PRESIDENT

M. BERTRAND
C. FEUGEAS
G. POUZARD

} EXAMINATEURS

H. CHRISTOL
G. MAVEL

} INVITES



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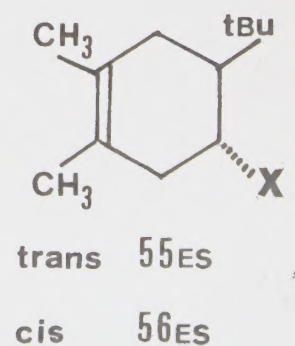
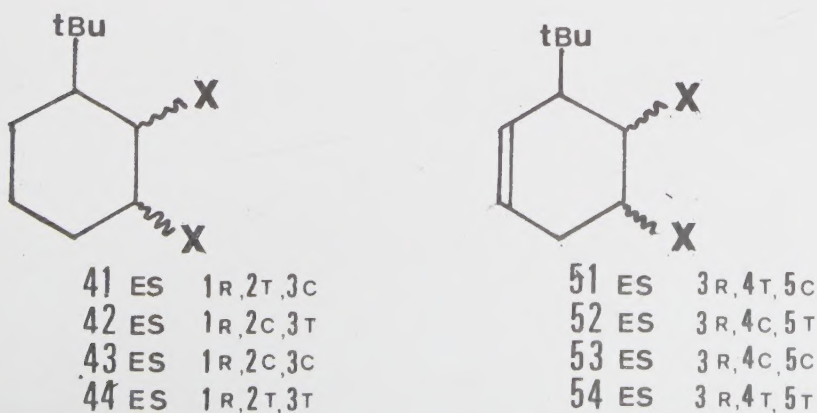
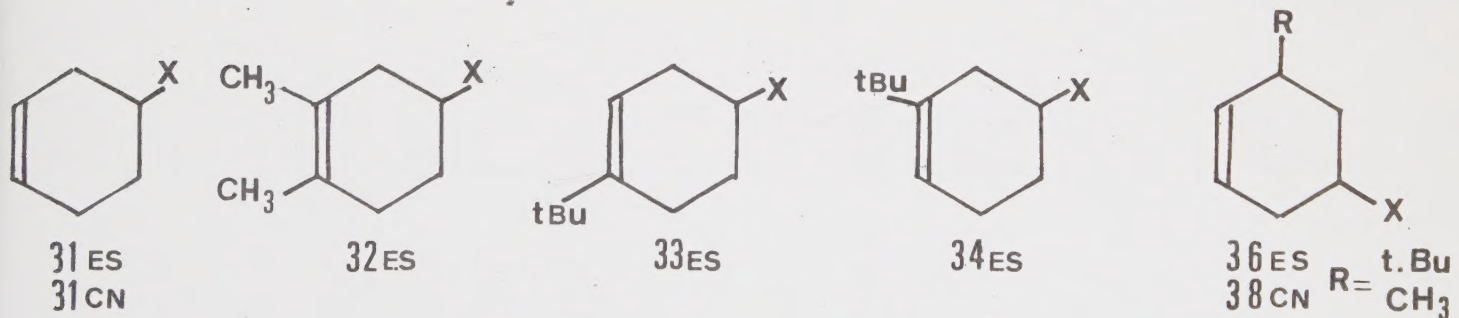
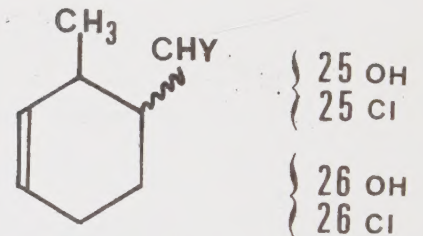
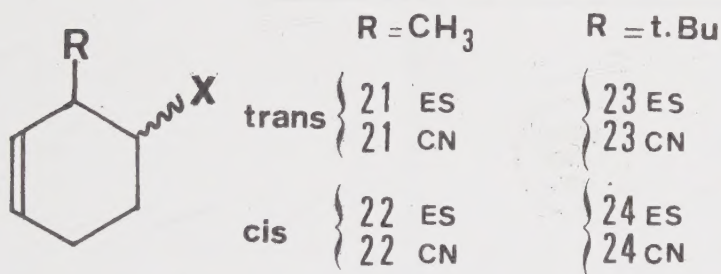
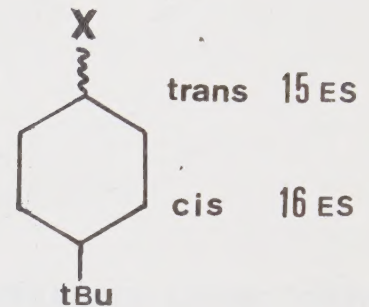
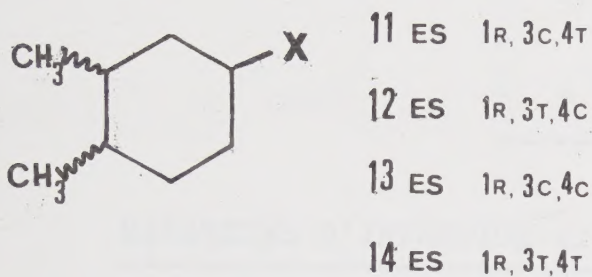
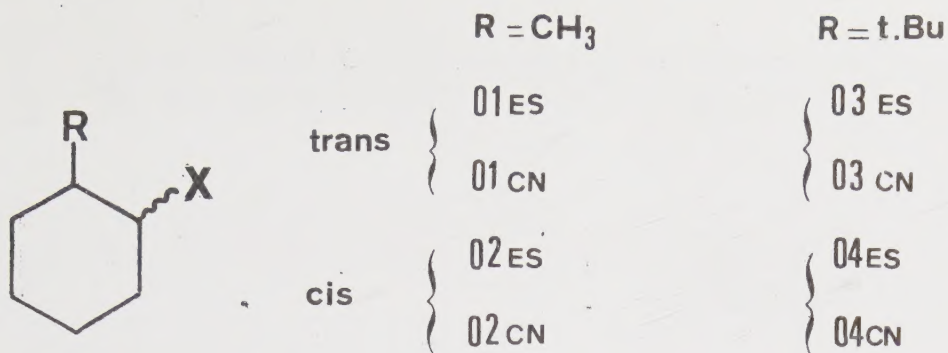
} EXAMINATEURS

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G. MAVEL

} INVITES



Tableau II, 2 : Classement des composés

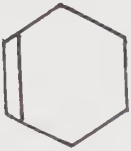
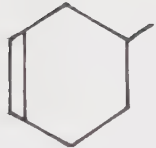
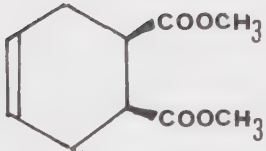
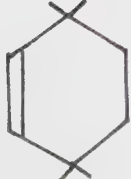


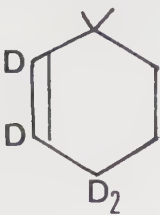
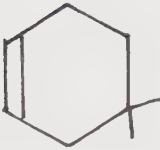
- A N N E X E I -

BARRIERES D'INVERSION ET DIFFERENCES D'ENTHALPIE LIBRE CONFOR-
MATIONNELLE EN SERIE CYCLOHEXENIQUE.

BARRIERES D'INVERSION DES COMPOSES CYCLOHEXENIQUES

(kcal.mole⁻¹).

Composé	$\Delta G^\ddagger$	Méthode (T°C)	Référence
	6,9 ^{a)}	calculs	(1)
	5,93 ^{a)}	calculs	(2)
	5,3	R.M.N. (-164)	(3)
	5,37 ± 0,1	R.M.N. (-166,7)	(4)
 F ₁₀	6,28	R.M.N. (-124)	(5)
	F { 5,30 ± 0,1	R.M.N. (-151,8)	(4)
	Cl { 6,3 ± 0,1	R.M.N. (-151,8)	(4)
	Br { 6,3 ± 0,1	R.M.N. (-149,3)	(4)
	I { 6,5 ± 0,1	R.M.N. (-146,3)	(4)
	7,4 ± 0,1	R.M.N. (-135,5)	(4)
	8,4	R.M.N. (-117)	(6)

Composé	$\Delta G^\ddagger$	Méthode (T°C)	Référence
	6,3	R.M.N.(-146,8)	(6)
	6,1	R.M.N.(-155,2)	(6)

a) $\Delta E^\ddagger$

DIFFERENCES D'ENTHALPIE LIBRE CONFORMATIONNELLE

(ΔG_X° en kcal.mole⁻¹) EN SERIE CYCLOHEXENIQUE.

X	Position	$-\Delta G_X^\circ$	Méthode (T°C)	Référence
F	4	+0,014 $\pm$ 0,005	R.M.N. (-160°)	(4)
Cl	3	-0,64	I.R.	(7)
	4	+ 0,2 $\pm$ 0,01	R.M.N. (-157°)	(4)
	4	+ 0,2	R.M.N.	(8)
	4	+ 0,2	I.R.	(9)
Br	3	- 0,64	I.R.	(7)
	4	- 0,05	I.R.	(10)
	4	+ 0,077 $\pm$ 0,015	R.M.N. (-157°)	(4)
I	4	- 0,016 $\pm$ 0,007	R.M.N. (-157°)	(4)
OH	3	+ 0,4	Epimérisation	(11)
OCH ₃	3	0,0	Epimérisation	(11)
$\text{O}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{CH}_3 \end{array}$	3	0,0	Epimérisation	(11)
CH ₃	3	+ 0,6	R.M.N.	(12)
	3	> 0	Epoxydation	(13)
	3	+ 0,76	Calculs	(15)
	4	+ 1	Epoxydation	(13)

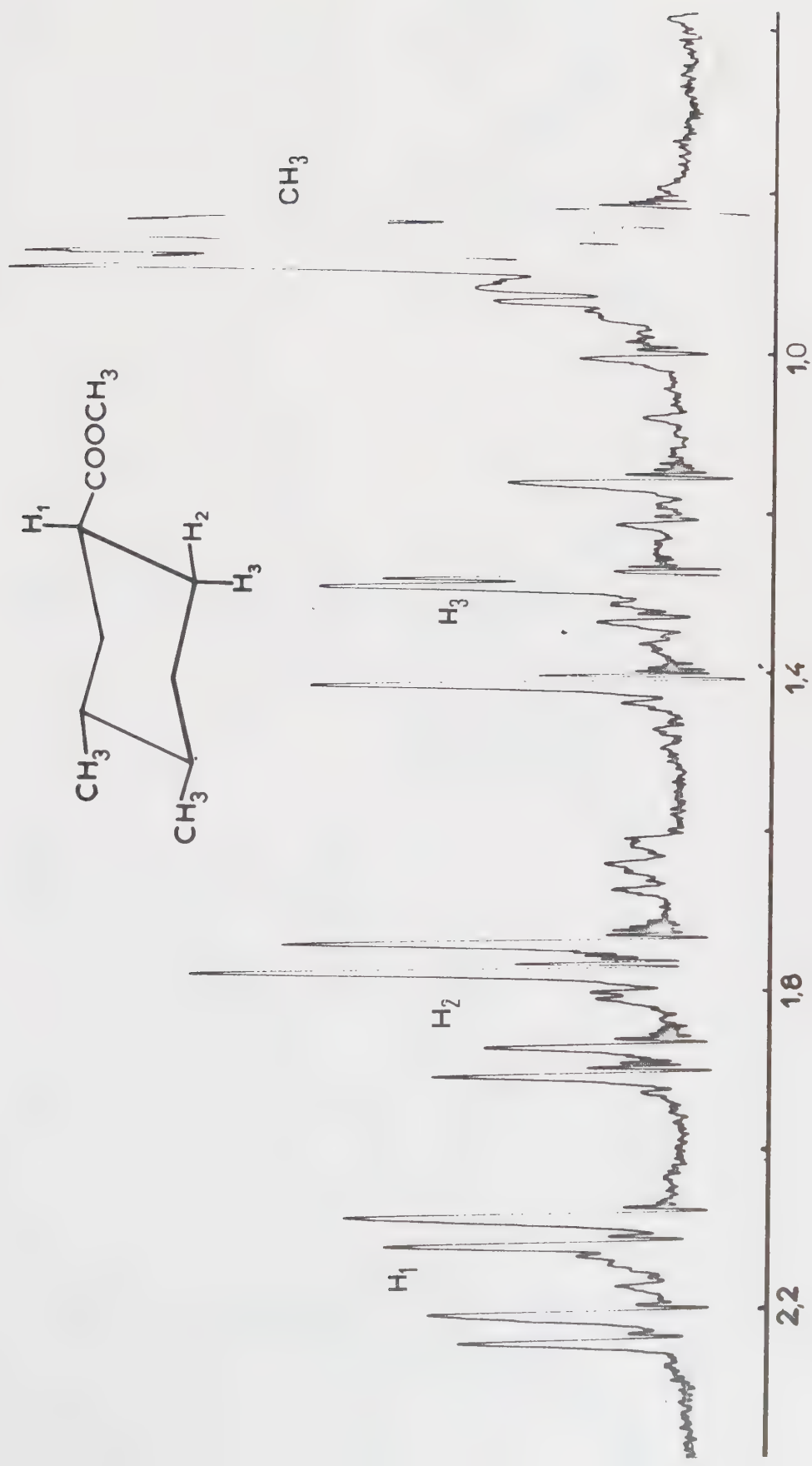
X	Position	ΔG_X°	Méthode (T°C)	Référence
CD ₃	4	+ 0,85	R.M.N.	(14)
C ₆ H ₅	4	+ 0,848 ($-\Delta H_X^\circ$)	R.M.N.	(14)
	4	+ 1,23	R.M.N. (133°)	(14)
CD ₂ OH	4	+ 0,92	R.M.N.	(14)
CD ₂ OAC	4	+ 0,86	R.M.N.	(14)
CHO	4	+ 0,4	R.M.N.	(15)
COC ₆ H ₅	4	+ 0,4	R.M.N.	(15)
CO ₂ H	4	+ 0,83	R.M.N.	(14)
	4	+ 1,0	R.M.N.	(15)
	4	+ 1,0	R.M.N.	(16)
CO ₂ CH ₃	4	+ 0,8	R.M.N.	(15)
CO ₂ C ₂ H ₅	4	+ 0,85	R.M.N.	(14)
	4	+ 1,0	R.M.N.	(8,16)
C(CH ₃) ₂ OH	4	+ 2,18	R.M.N.	(14)
C(CH ₃) ₂ OCH ₃	4	+ 2,94	R.M.N.	(14)
CN	4	0,0	R.M.N.	(8)
	4	+ 0,1	R.M.N.	(15)
NO ₂	4	+ 0,2	R.M.N.	(15)

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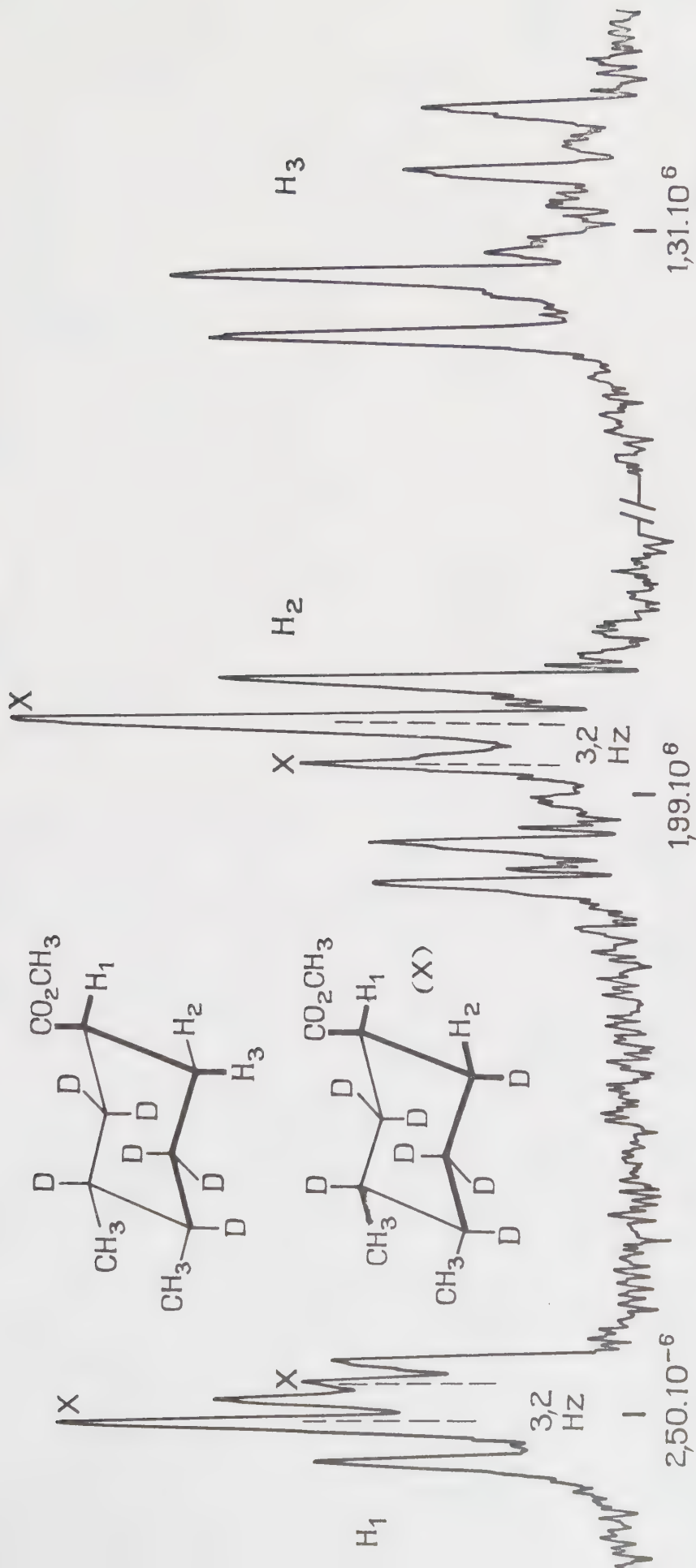
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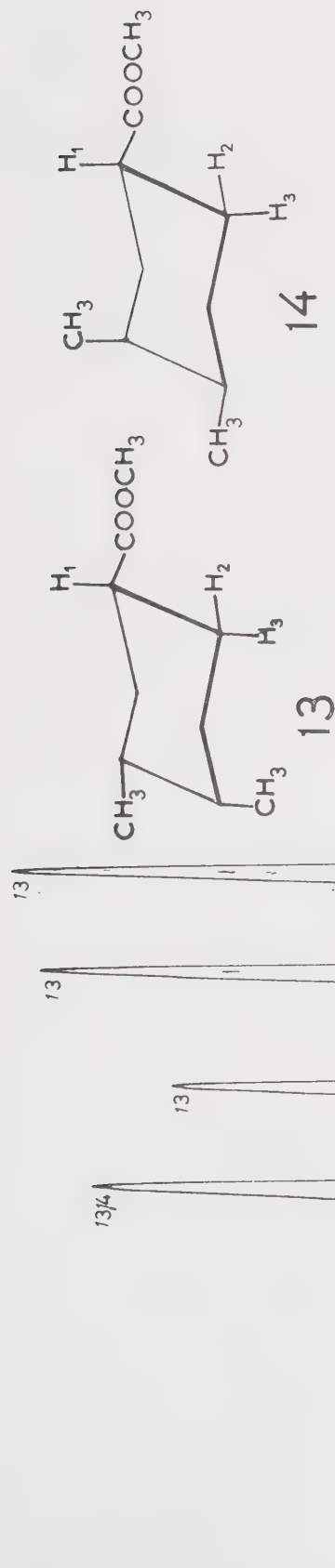
SPECTRES DE R.M.N.



autre signal

$\delta_{\text{COOCH}_3} = 3,5$





B

2,4 2,2 2,0

x 13ES D_{7-6e}

A

1,8 1,6 1,4 1,2

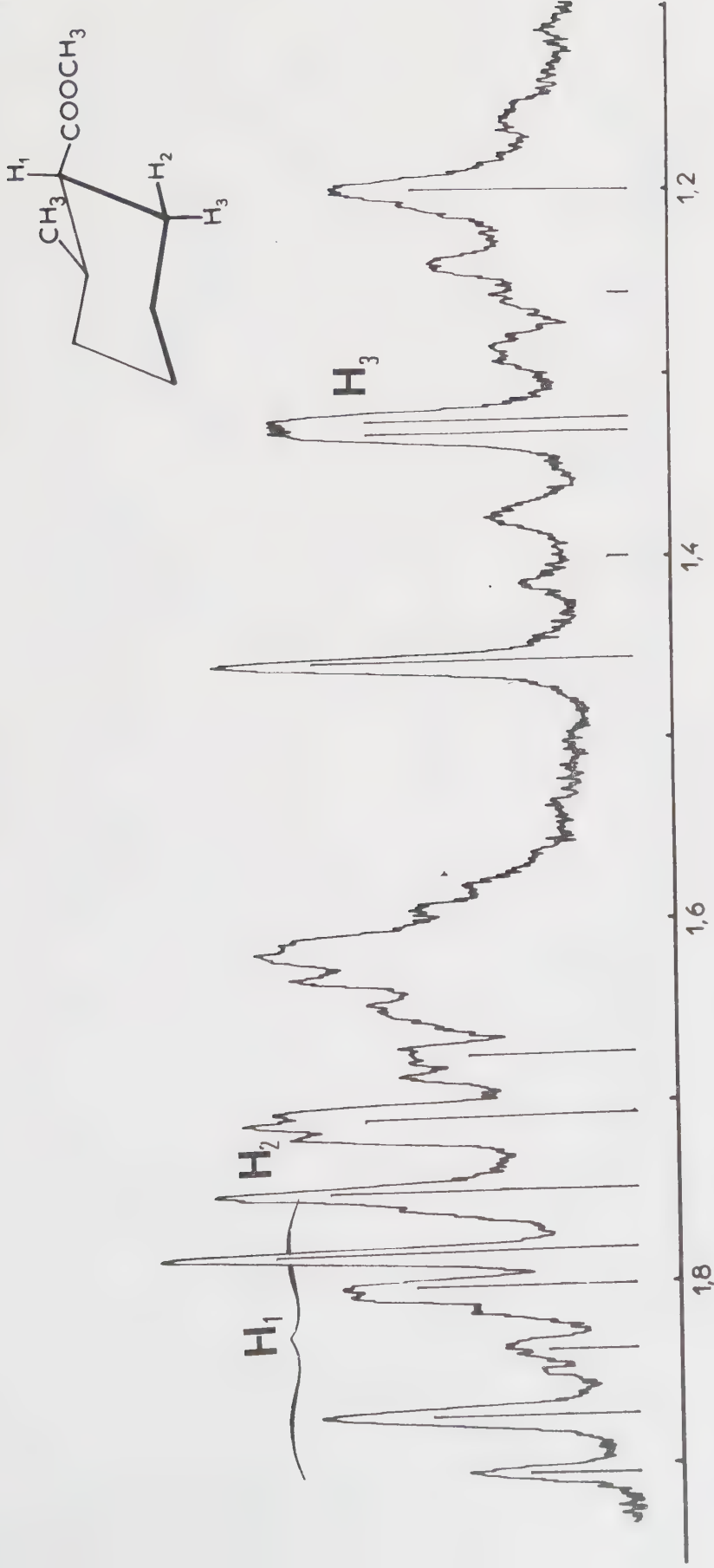
A H₂ et H₃
B H₁

n°04

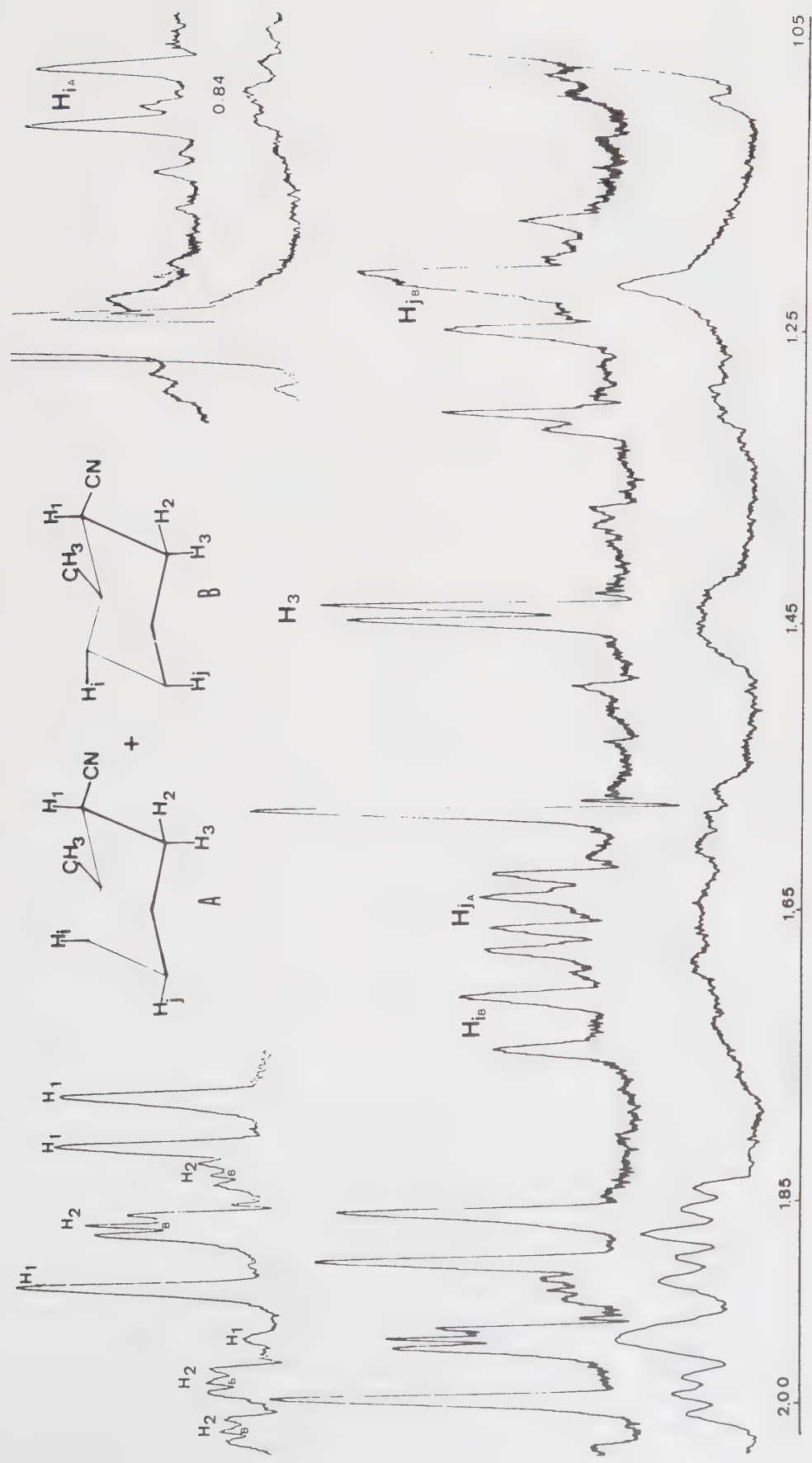
autres signaux

$$\delta \text{CH}_3 = 0,8$$

$$\delta \text{CO}_2\text{CH}_3 = 3,53$$



Méthyl 1-2 méthoxycarbonylcyclohexane D₅-2,3,4,5,5 trans 01ES



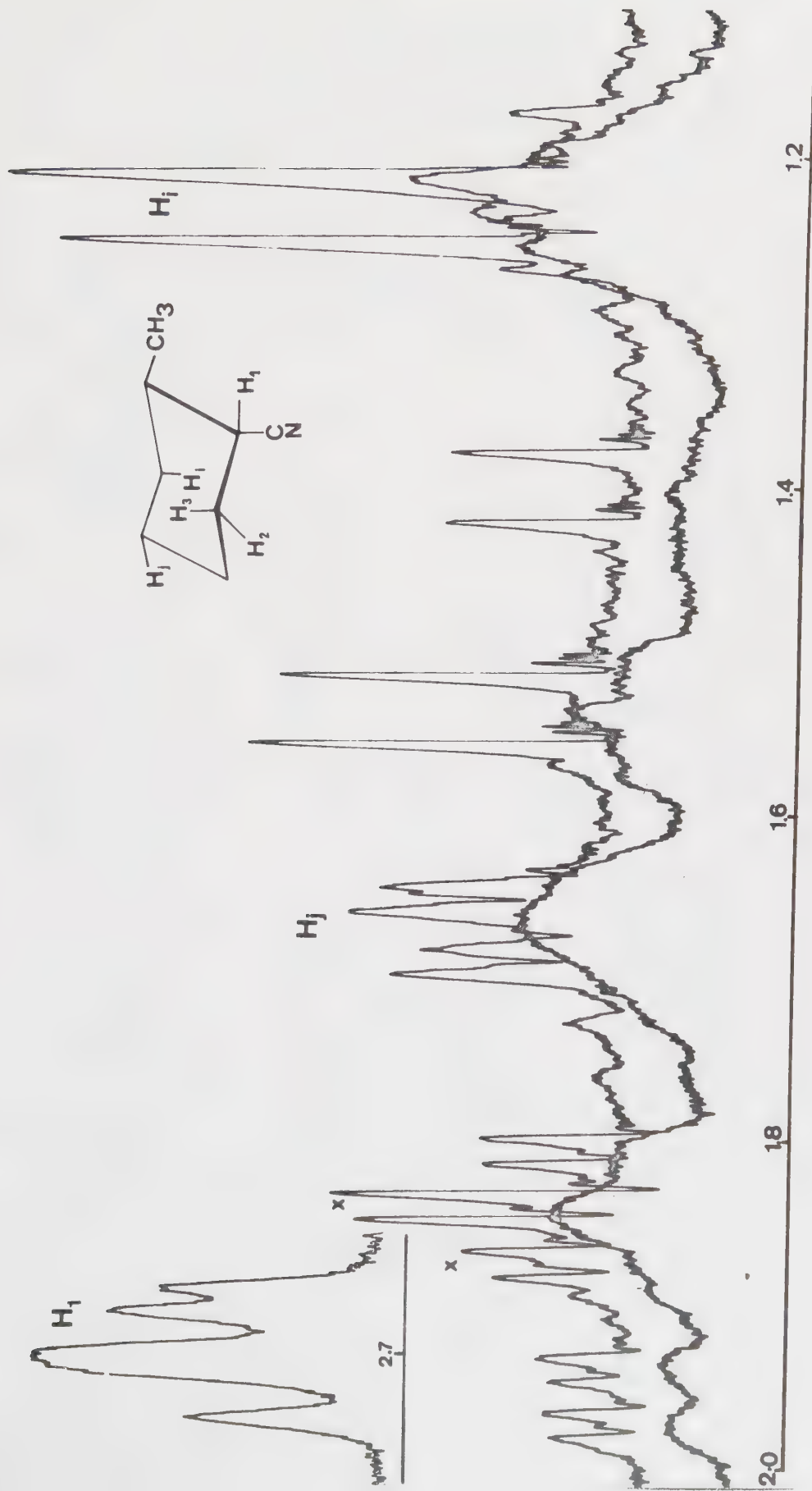
Méthyl-2 cyanocyclohexane D_5 2,3,4,5,5 trans 02 CN

n°06

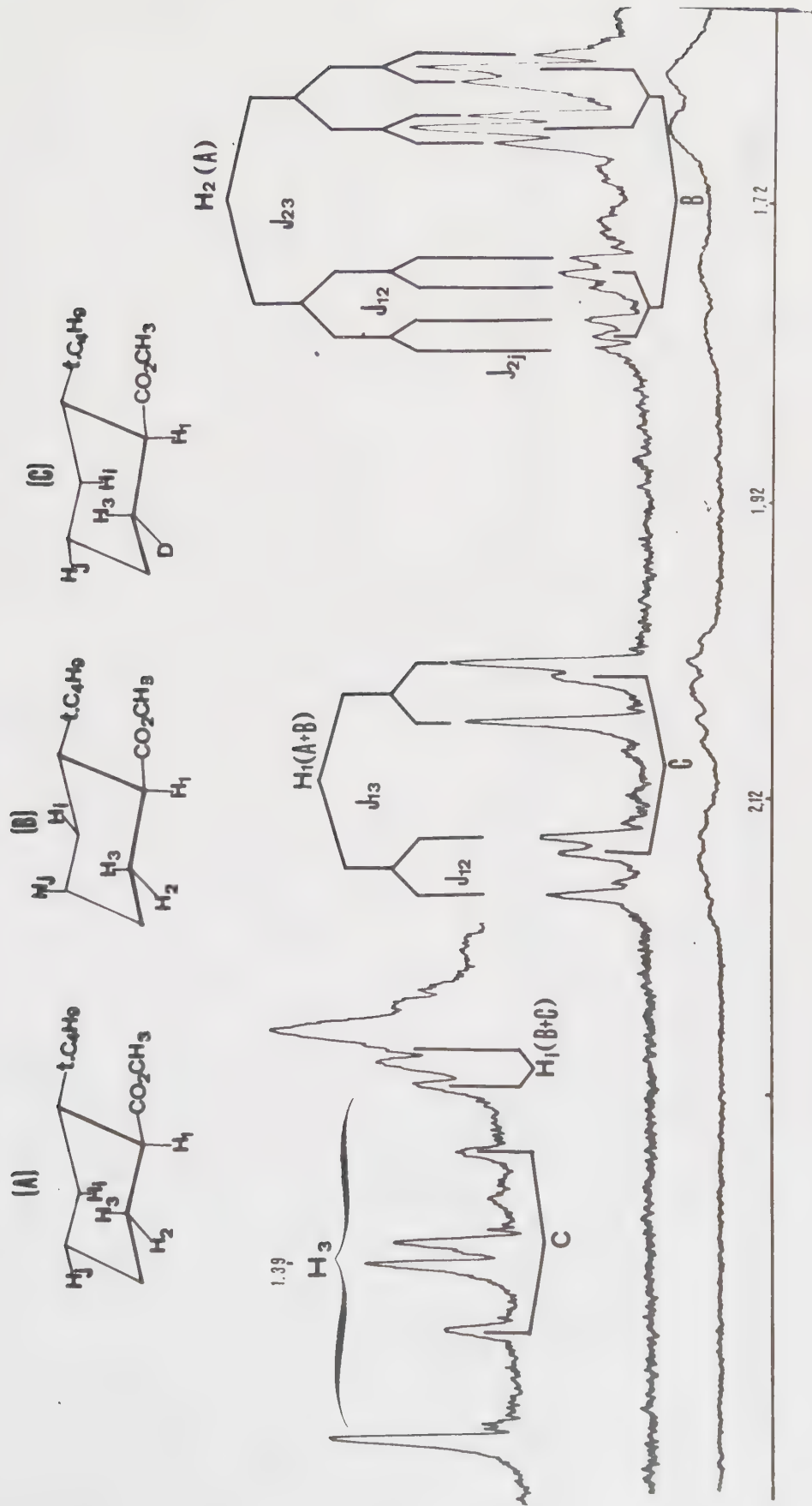
x 02CN D₆-6a

autre signal

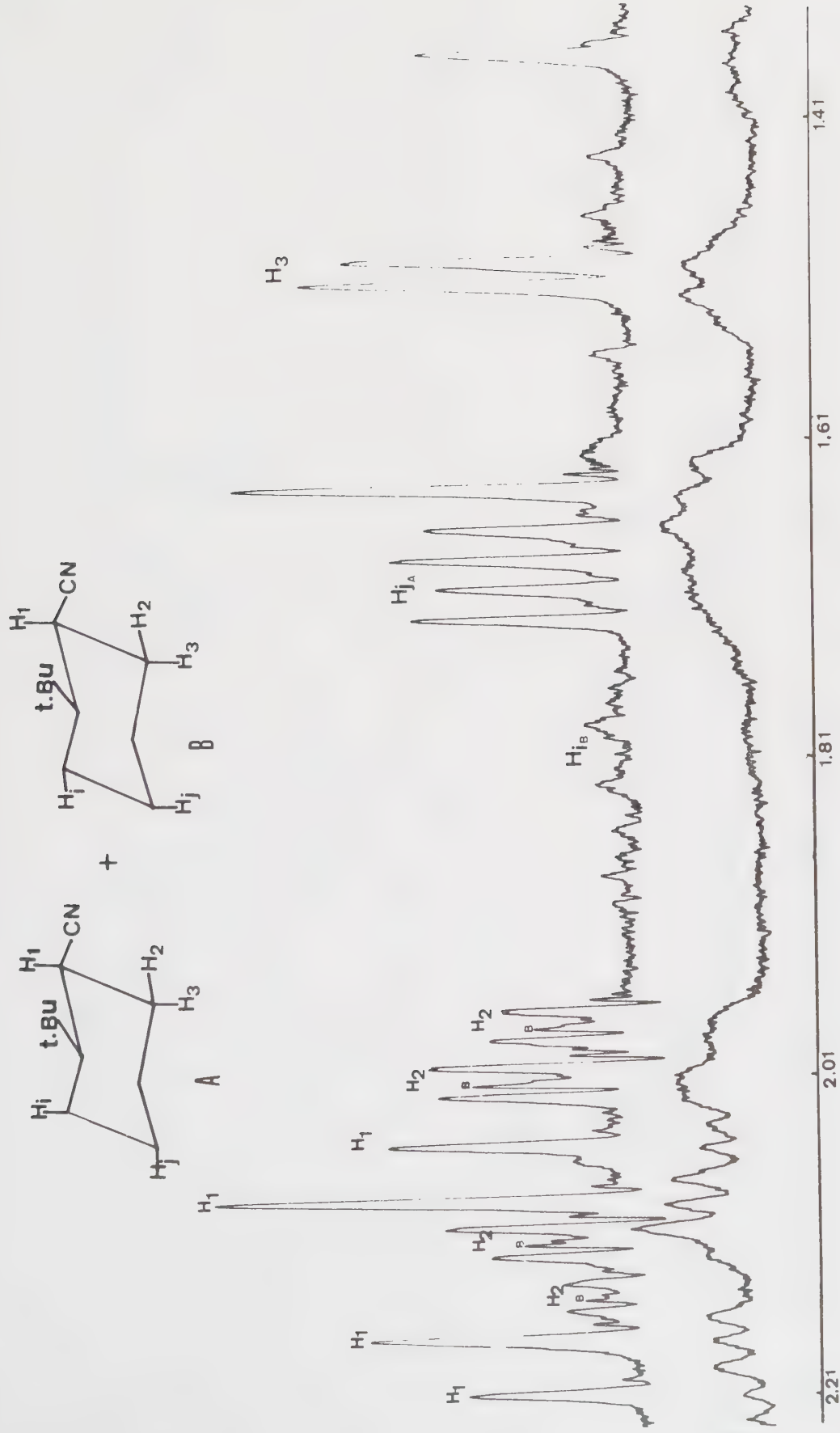
$\delta\text{CH}_3 = 10.3$



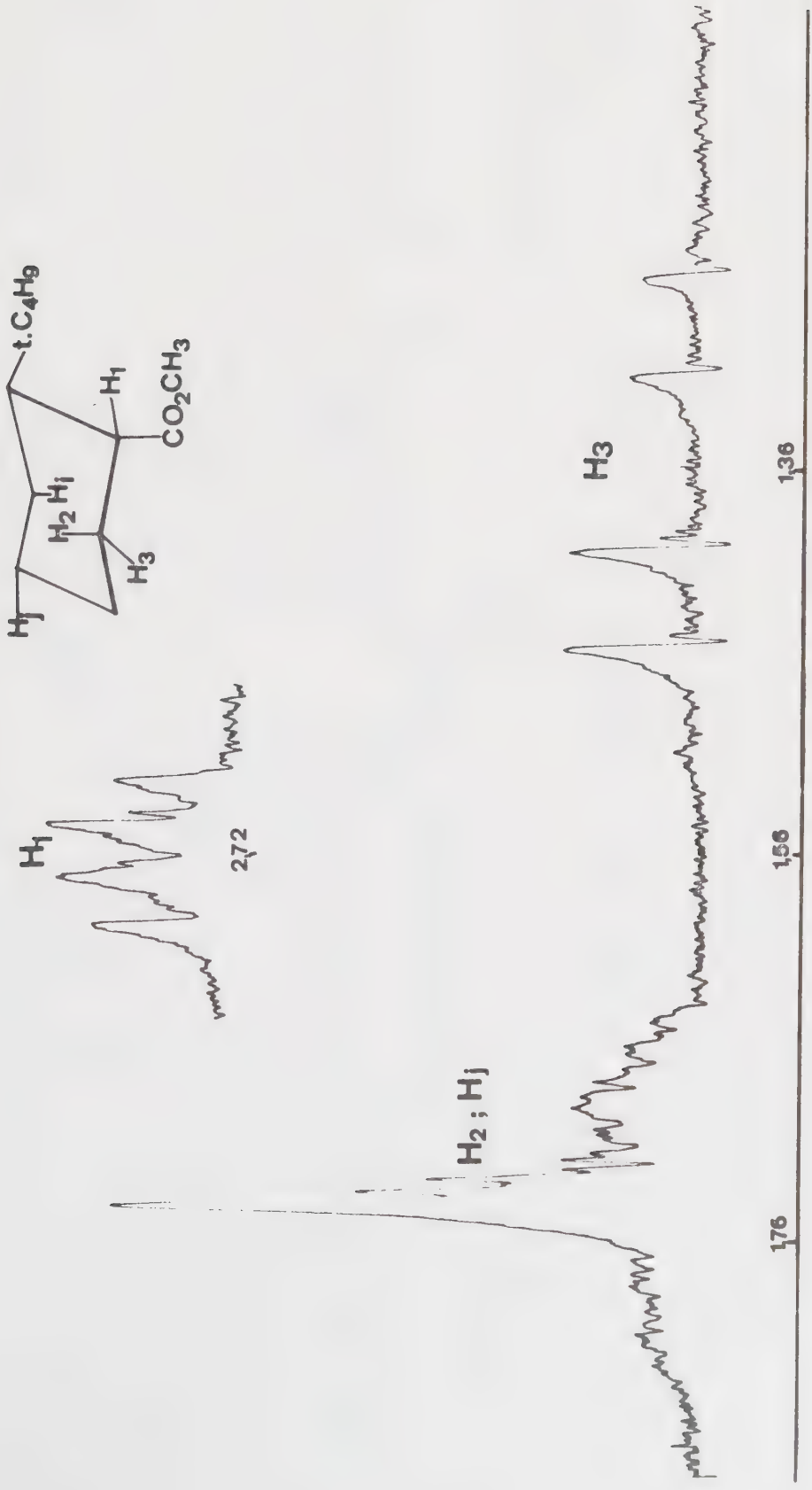
Méthyl-2 cyanocyclohexane D₆-2 3 4 5 5 cis 02CN



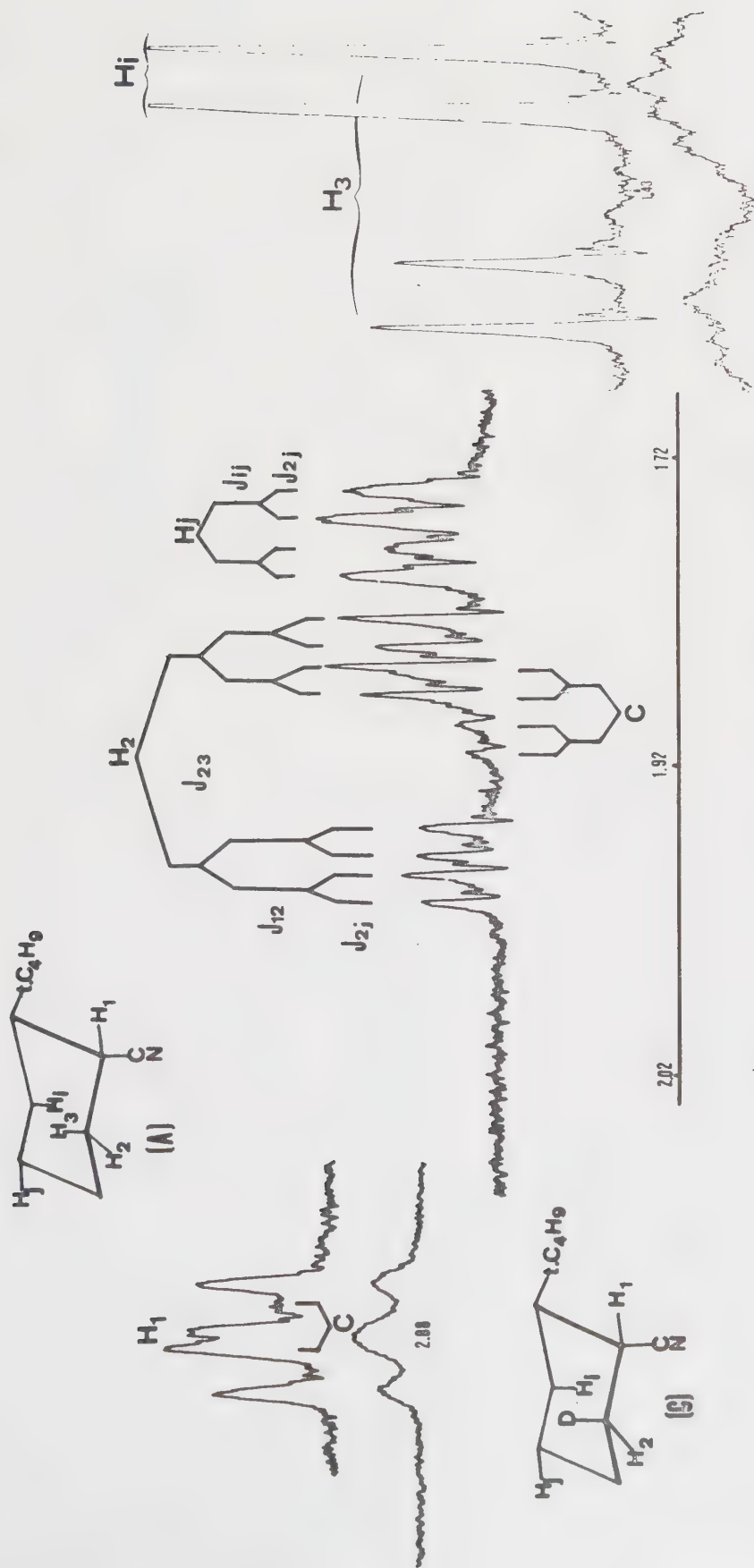
T.butyl-2 méthoxycarbonylcyclohexane D₅-2,3,4,5,5 trans 03ES



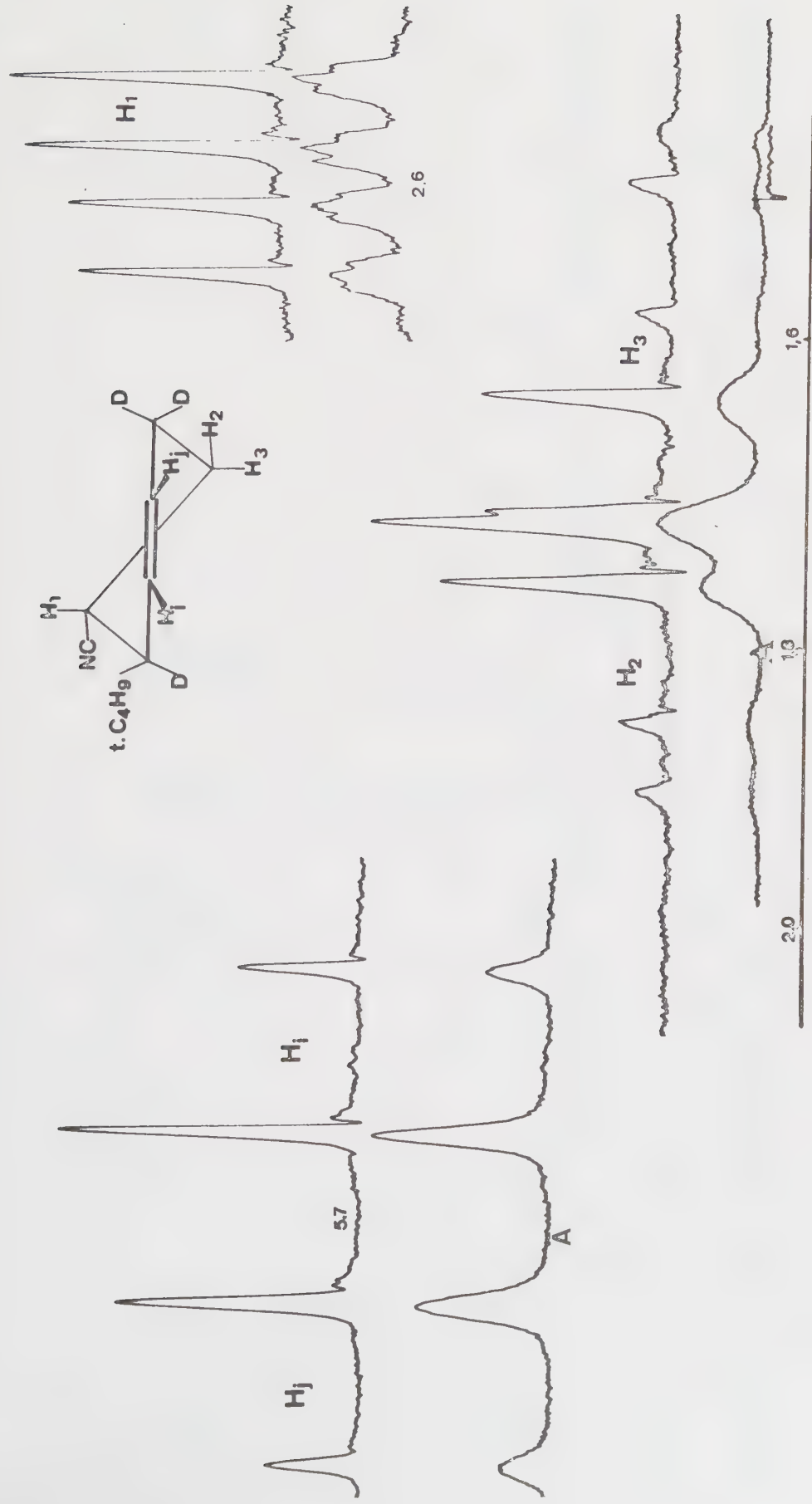
T-butyl-2 cyanocyclohexane D₅-2,3,4,5,5 trans 03CN



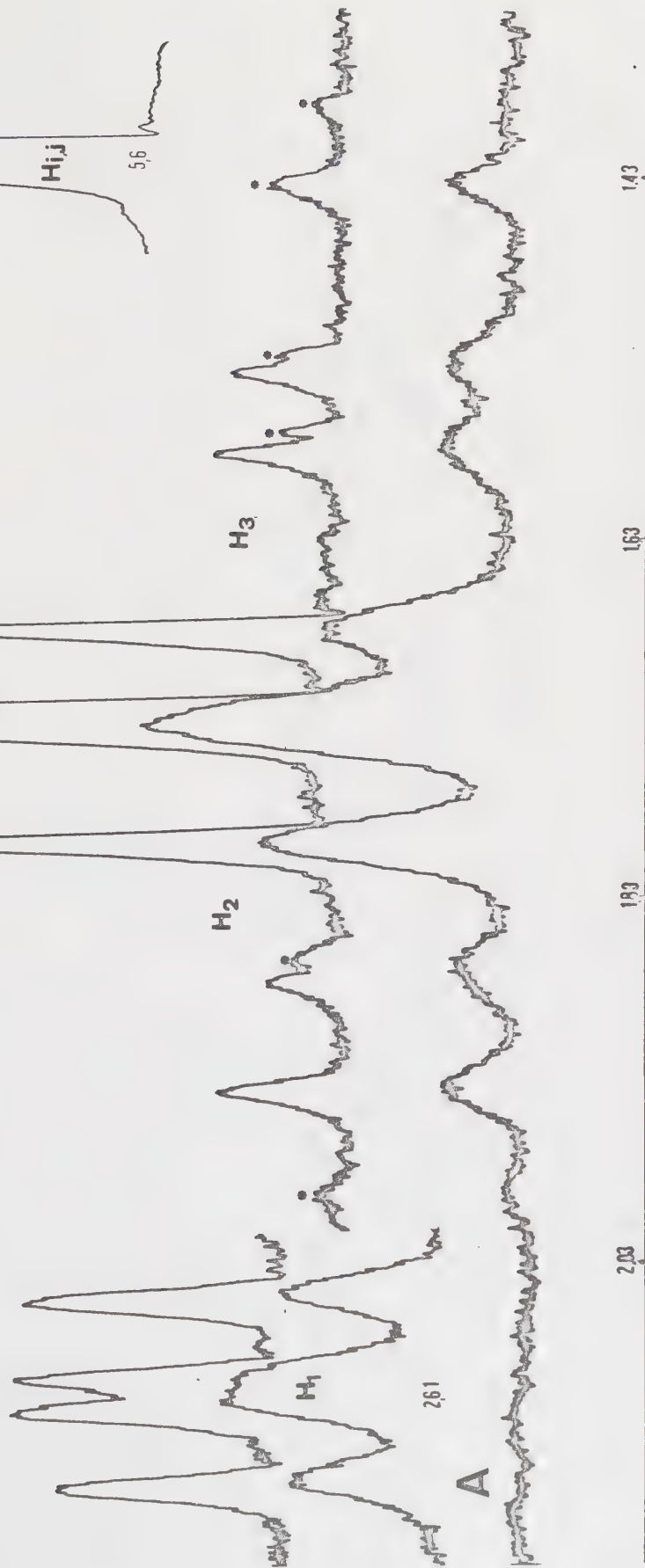
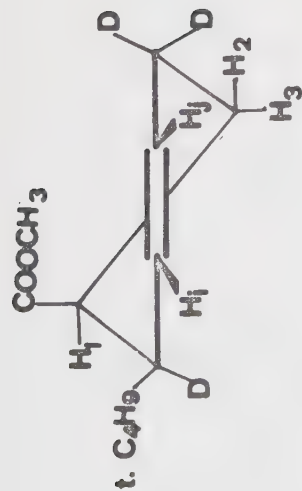
T-butyl-2 méthoxycarbonylcyclohexane D_5 -2,3,4,5,5-cis 22ES



T-butyl-2-cyanocyclohexane D₅-2,3,4,5,5 cis 04CN

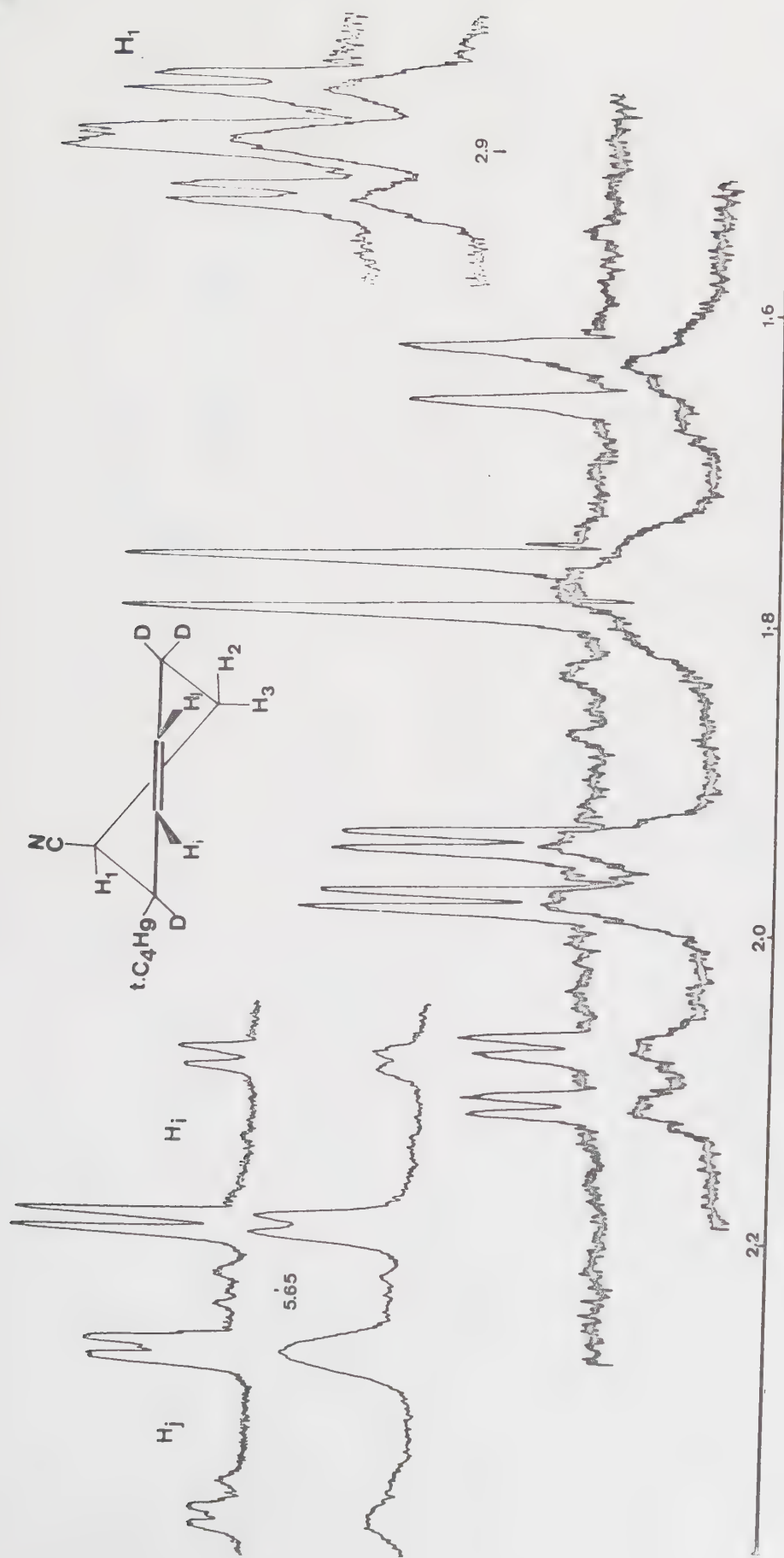


Cyano - 4 t.butyl-3 cyclohexène $\text{D}_3,6,6$ trans ^{13}C N

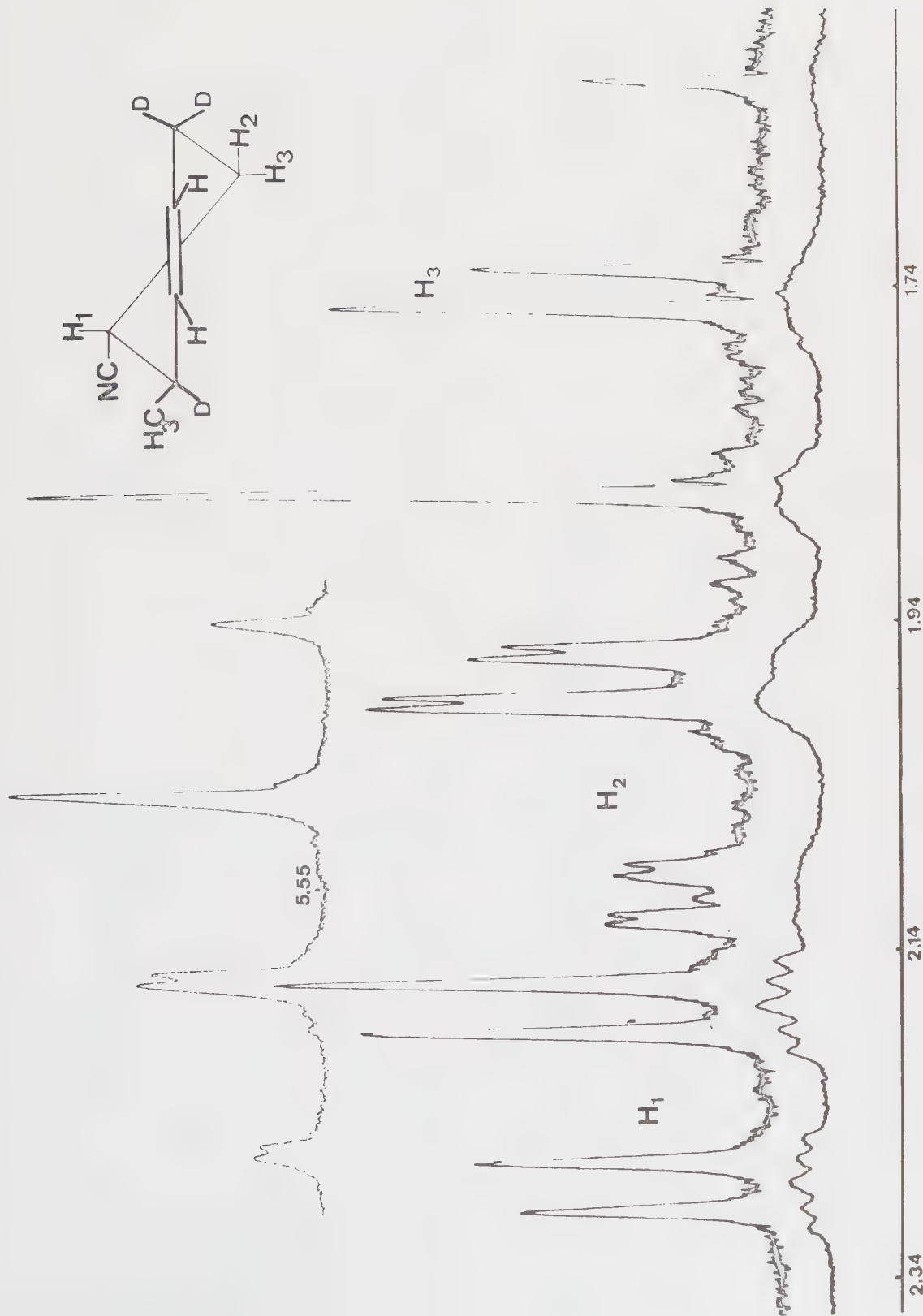


A) sans irradiation du deutérium

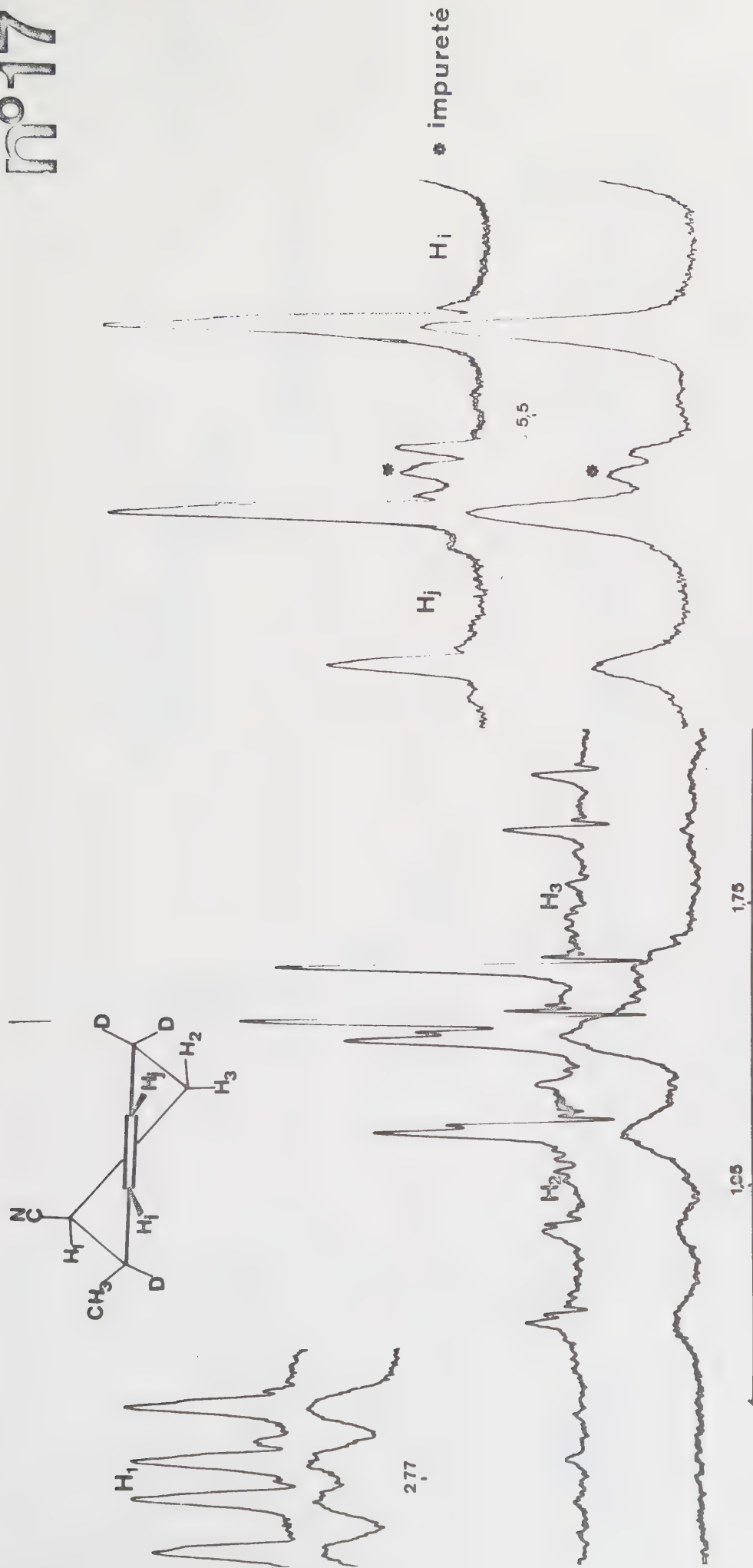
Métoxycarbonyl-4 t-butyl-3 cyclohexèneD₃-3,6,6 cis 24ES



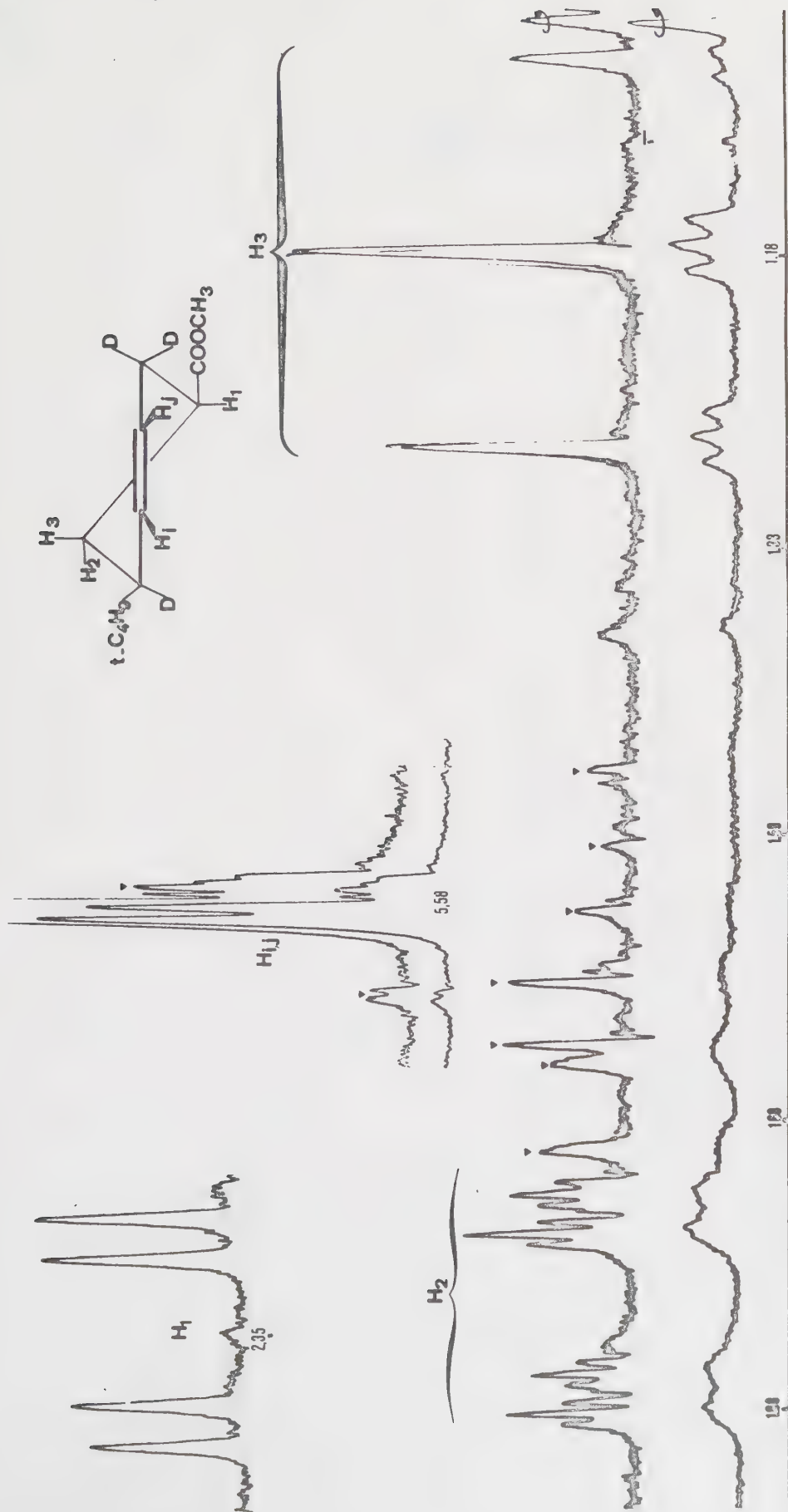
Cyano-4 t-butyl-3 cyclohexène D₃-3,6,6 cis 24CN



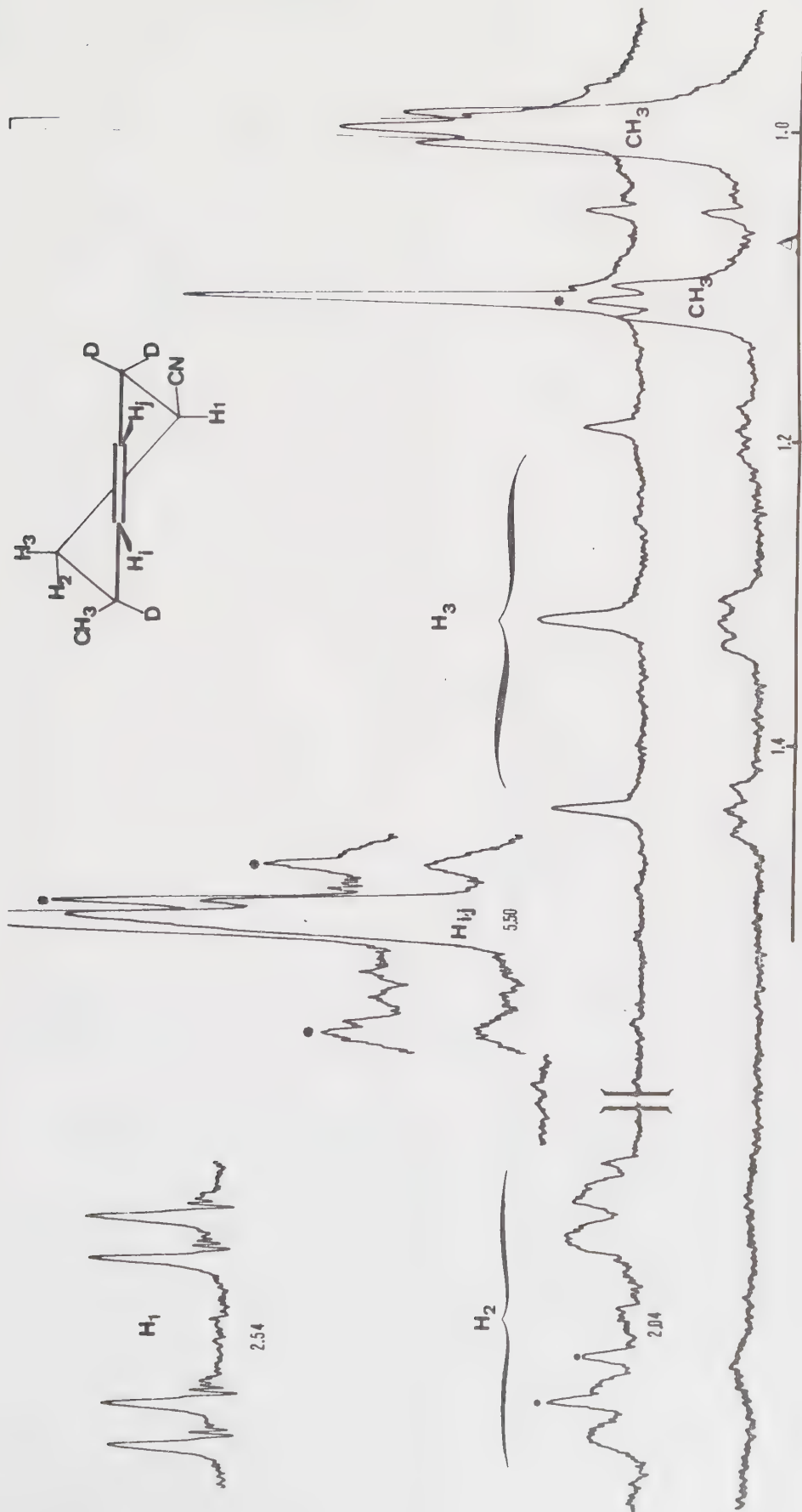
Cyano-4 méthyl-3 cyclohexène D_3 -3,6,6 trans 21CN



Cyano-4 méthyl-3 cyclohexène D₃-3,6,6 cis 22 CN



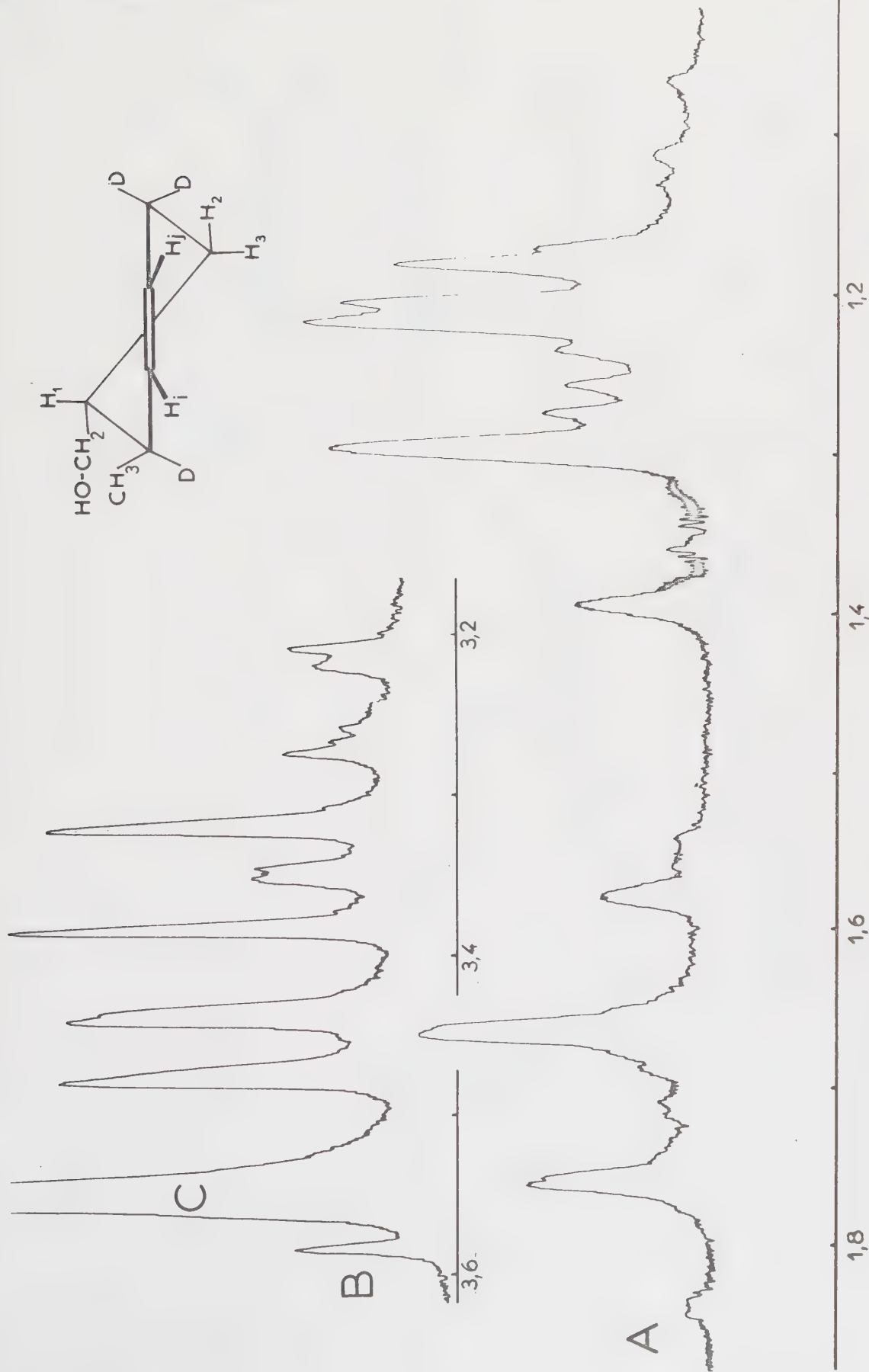
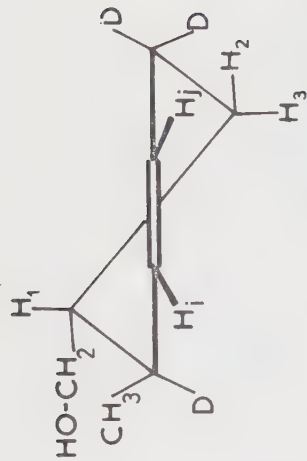
Méthoxycarbonyl-5 t-butyl-3 cyclohexène D_3 -3,6,6 cis 36ES



* impureté ^2H CN

Cyano-5 méthyl-3 cyclohexène D_3 -3,6,6 cis 38CN

n°21



A H₁ H₂ H₃

B CH₂O

C OH

solvant

CCl₄

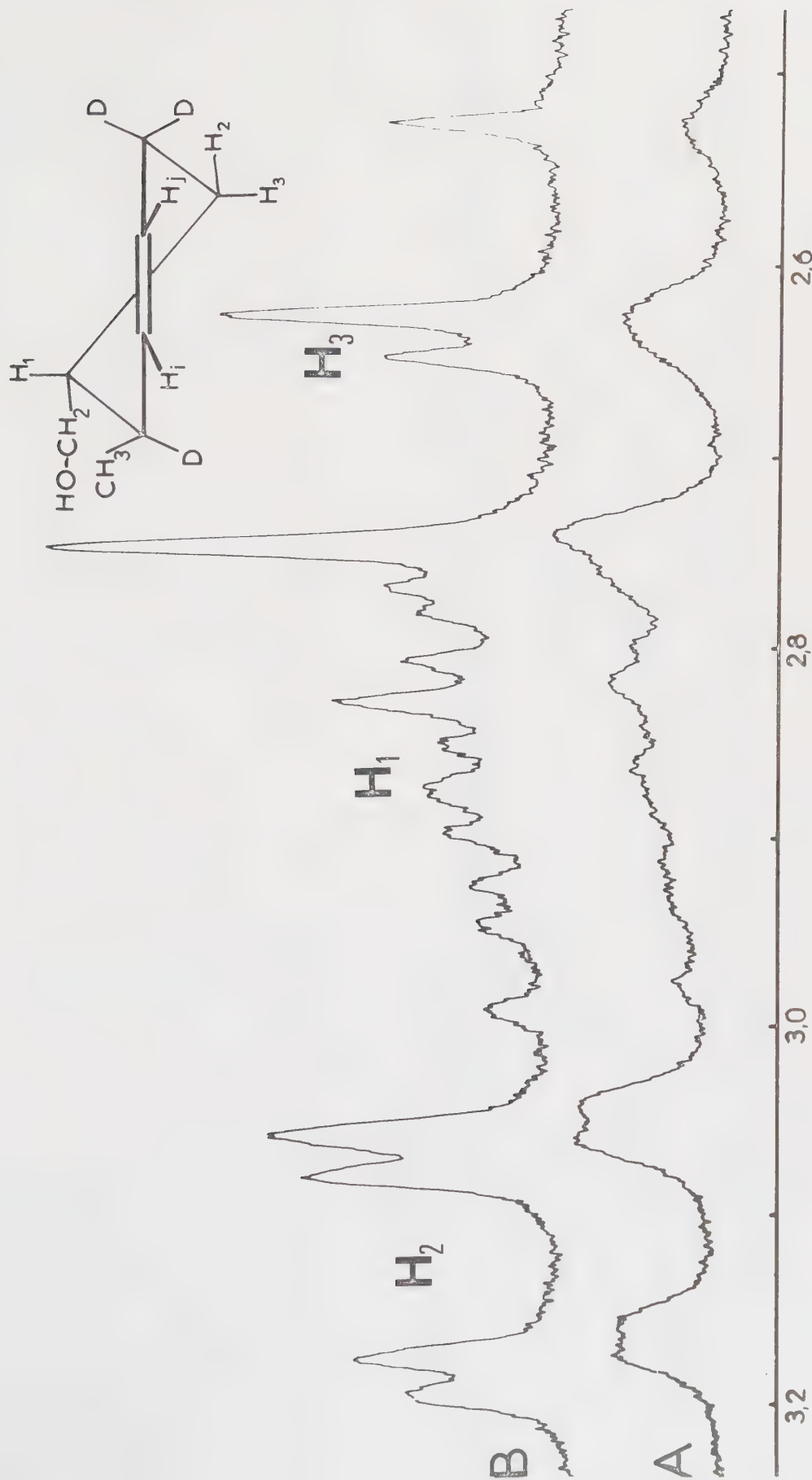
autres signaux

$\delta_{CH_3} = 0.95$

$\delta_{H_i} = 5.35$

$\delta_{H_j} = 5.50$

Hydroxyméthyl-4 méthyl-3 cyclohexène D₃ 3,5,5 trans 250H

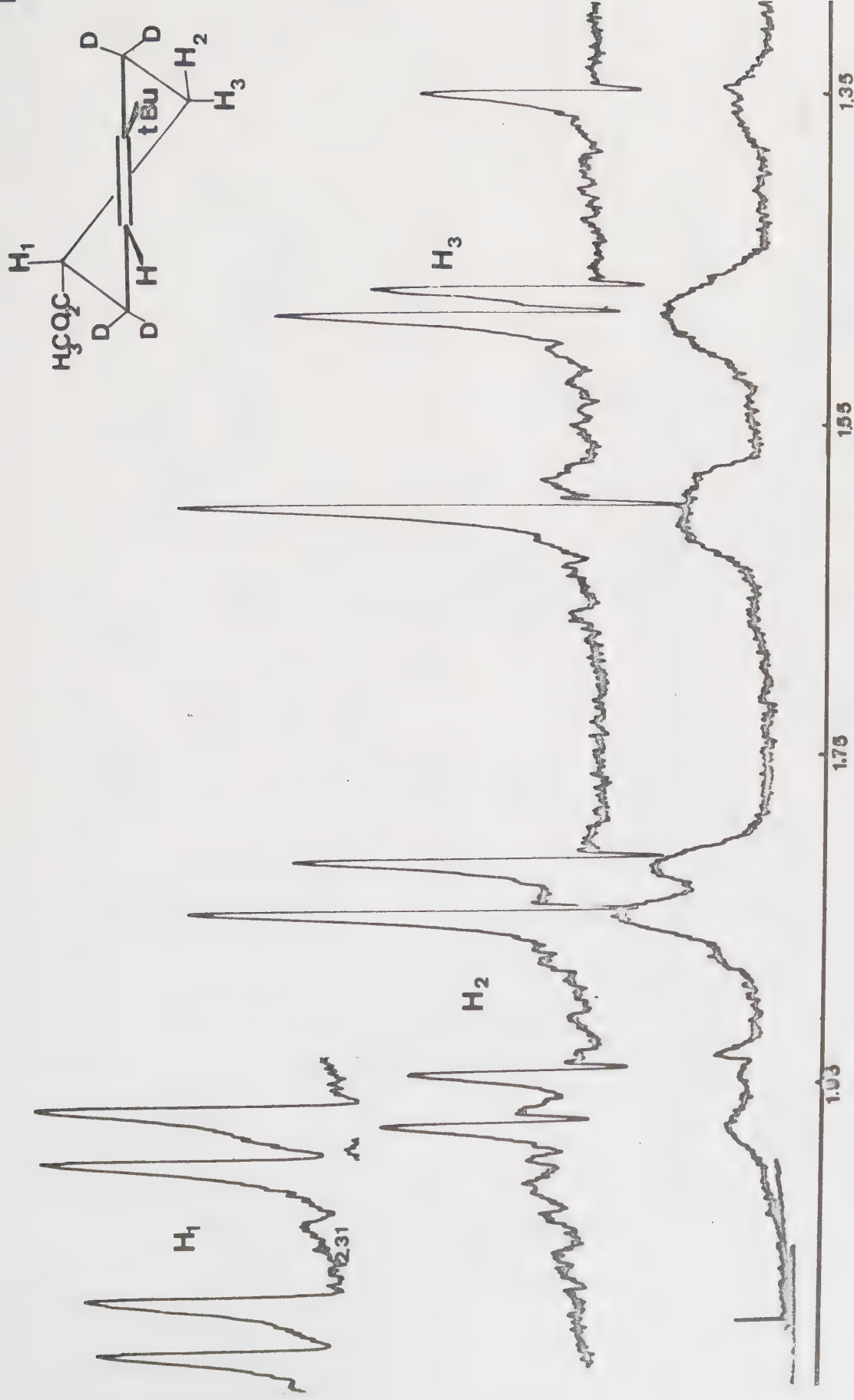


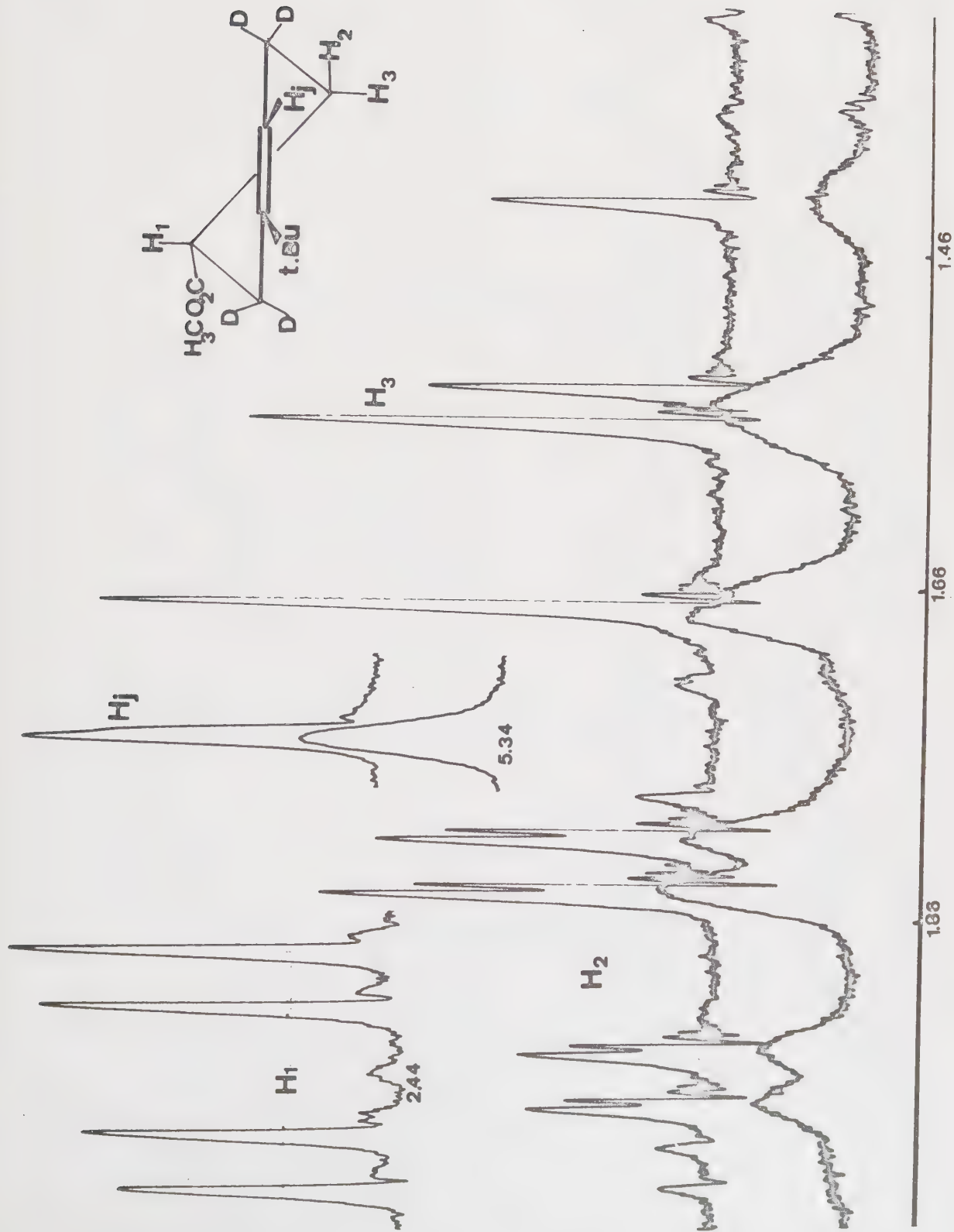
solvant CCl₄

$$\frac{M}{L} = 1,3 \cdot 10^{-3}$$

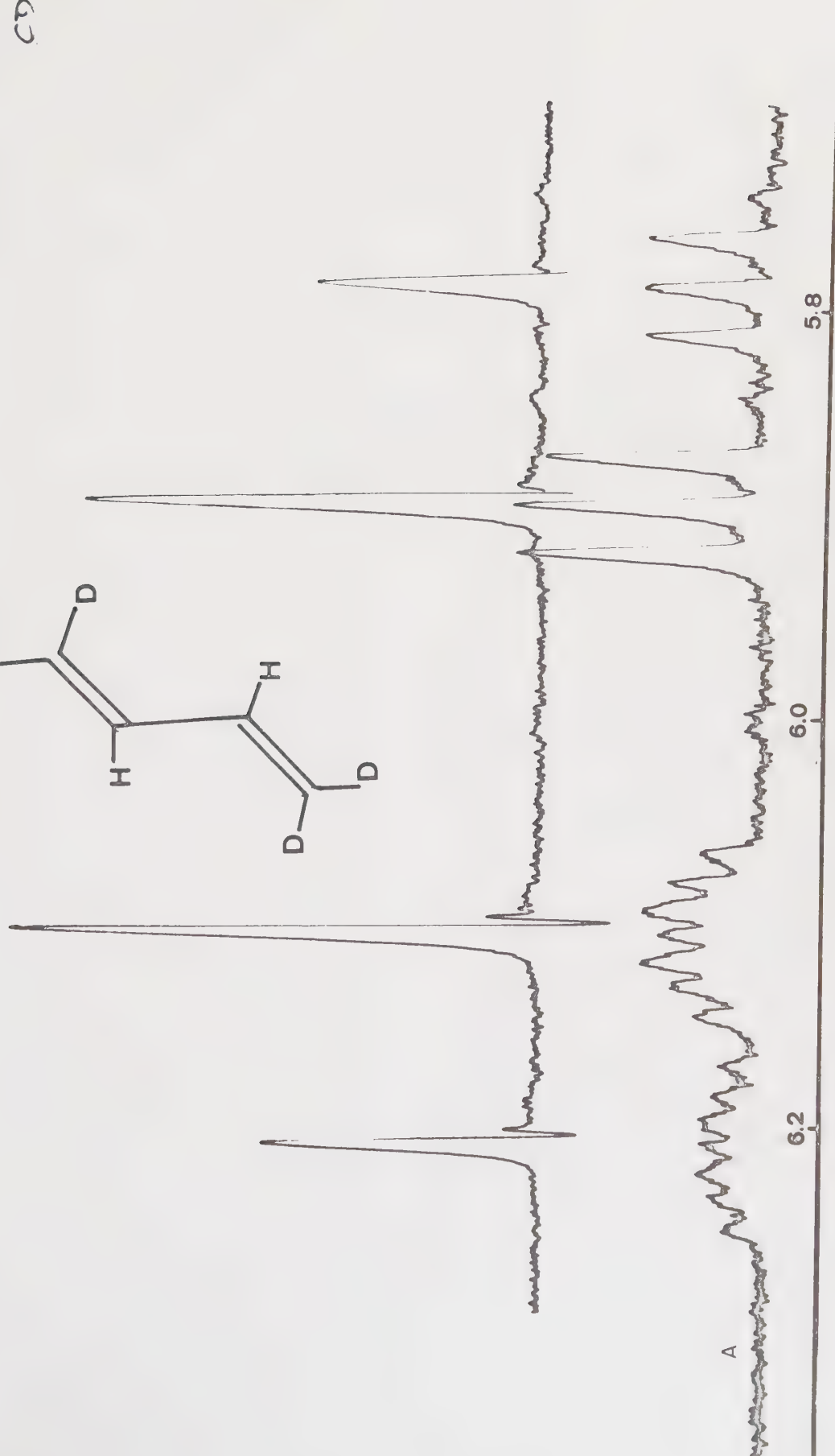
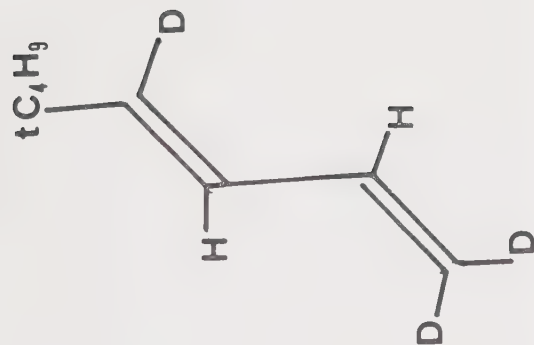
Hydroxyméthyl-4 méthyl-3 cyclohexène D₃-3,5,5 trans 250H

A avec irradiation du deutérium
B sans irradiation du deutérium





CD



t-bu-1,3D₂-1,4,4D₃

A - sans irradiation du deutérium

VU ET PERMIS D'IMPRIMER

MARSEILLE, le

LE PRESIDENT DE L'UNIVERSITE DE PROVENCE

F. BOREL

